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Natural Gradient Experiment on Solute Transport in a Sand Aquifer 4. Sorption of Organic Solutes and Its Influence on Mobility

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16. ABSTRACT

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A Natural Gradient Experiment on Solute Transport in a Sand Aquifer
4. Sorption of Organic Solutes and its Influence on Mobility

GARY P. CURTIS, PAUL V. ROBERTS, AND MARTIN REINHARD

Department of Civil Engineering, Stanford University, Stanford, California

Laboratory investigations were conducted to determine whether the observed field retardation of bromoform, carbon tetrachloride, tetrachloroethylene, 1,2-dichlorobenzene, and hexachloroethane at the Borden field site could be explained by the linear, reversible, equilibrium sorption model. The five halogenated organic solutes, which have octanol-water partition coefficients ranging from 200 to 4000, were the same as those used in the field study. The sorbent, a medium sand containing 0.02% organic carbon, was excavated 11.5 m from the experimental well field at the Borden site. Sorption isotherms were linear in the aqueous concentration range from 1 to 50 μg/L and could be described by a single distribution coefficient K_d. The experimentally determined K_d exceed those predicted by the hydrophobic sorption model that accounts only for partitioning into organic matter, by factors ranging from 1.7 for hexachloroethane to 10 for tetrachloroethylene. Retardation factors inferred from the laboratory-determined distribution coefficients fell within the range estimated from spatial sampling data in the field experiment.

INTRODUCTION

Transport of nonpolar halogenated organic solutes in groundwater may be affected by advection, dispersion, sorption, and either biological or chemical transformations. To obtain a sufficiently detailed data base to delineate among these various processes under field conditions, a 2-year experiment was conducted at Canadian Forces Base Borden in Ontario, Canada. Previous papers in this series presented details on the design and implementation of the experiment [*Mackay et al.*, this issue], an analysis of the field transport of the inorganic tracers chloride and bromide [*Freyberg*, this issue], and analysis of the field transport of halogenated organic solutes [*Roberts et al.*, this issue]. Transport of both chloride and bromide was essentially conservative [*Freyberg*, this issue], while transport of the halogenated organic solutes varied widely in terms of retardation and in conservation of mass [*Roberts et al.*, this issue].

The two major objectives of this study are (1) to determine if the observed field retardation of carbon tetrachloride, bromoform, tetrachloroethylene, 1,2-dichlorobenzene, and hexachloroethane, agree with retardation estimated from sorption coefficients determined in batch laboratory experiments with core samples, and (2) to test the applicability of empirical correlations based on partitioning into organic matter for estimating sorption of slightly to moderately hydrophobic solutes onto a sandy aquifer material of low organic content.

BACKGROUND

Retardation Factor

The sorption isotherm of a given solute and aquifer material can be estimated by several experimental techniques, including measuring the relationship between the sorbed and aqueous concentrations by the batch equilibrium technique. This method has the advantage of directly establishing the linearity of the isotherm and, if a desorption isotherm is measured, the reversibility of the sorption. If the isotherm is linear and reversible, the isotherm is uniquely defined by a distribution coefficient K_d, which is constant and equal to the slope of the isotherm.

Several investigators have measured linear isotherms for sorption of nonionic organic solutes onto soils, sediments, and aquifer materials [*Chiou et al.*, 1979, 1983; *Karickhoff et al.*, 1979; *Means et al.*, 1980; *Brown and Flagg*, 1981; *Karickhoff*, 1981; *Schwarzenbach and Westall*, 1981]. These isotherms may be described by

$$q = K_d C_{eq} \tag{1}$$

where q (ng/g) and C_{eq} (ng/cm^3 or μg/L) are the sorbed and aqueous equilibrium concentrations, respectively. Results from such batch equilibrium sorption studies may be used for estimating the mobility of an organic solute in groundwater.

Estimates of Sorption

The migration of a sorbing solute in groundwater is retarded relative to the movement of a noninteracting tracer by a factor known as the retardation factor R [*Hashimoto et al.*, 1964; *Freeze and Cherry*, 1979]. The retardation factor for a linearly, reversibly, and independently sorbing but otherwise nonreacting solute at local equilibrium with a homogeneous, isotropic, saturated, porous medium with uniform steady flow is given by

$$R_i = 1 + \rho_b K_{di}/n \tag{2}$$

where ρ_b is the bulk density of the aquifer material (g/cm^3); n is the porosity (cm^3/cm^3); and K_{di} (cm^3/g) is the equilibrium distribution coefficient for solute i. Generally, for different soils and aquifer materials ρ_b and n do not vary to the extent that K_{di} varies: therefore R_i depends most strongly on K_{di}.

Numerous studies, recently sumarized by *Karickhoff* [1984], have shown that the distribution coefficient correlates well with the fraction of organic carbon (f_{oc}) of the sorbent resulting in the definition of an organic-carbon partition coefficient K_{oc} given by

$$K_{oc} = K_d/f_{oc} \tag{3}$$

For a given solute, this normalization typically reduces variations in K_d from several orders of magnitude to variations in

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K_{oc} of factors of 2 or 3, suggesting that K_{oc} for a given solute is weakly dependent on the source and nature of the sediment [*Karickhoff*, 1984].

K_{oc} also correlates well with both aqueous solubility S [*Chiou et al.*, 1979] and the octanol-water partition coefficient K_{ow} [*Karickhoff et al.*, 1979]. These correlations have led to the concept that the uptake of an organic solute by a natural sorbent proceeds by partitioning into the organic matter rather than by adsorption onto the mineral surfaces [*Chiou et al.*, 1979; *Karickhoff et al.*, 1979]. The mineral surfaces are presumed to be insignificant adsorbents for nonpolar organics because they are typically hydrophilic and therefore preferentially bind water [*Chiou et al.*, 1979]. The organic matter is believed to be a better sorbent for the nonpolar organic sorbates because it has pronounced hydrophobic character. The affinity of nonpolar organic solutes in aqueous solution for hydrophobic soil organic matter is in accord with the solvophobic theory of sorption [*Rao et al.*, 1985].

The direct correlation between K_{oc} and either K_{ow} or S has led to empirical methods of estimating K_d for a given solute-sorbent system. These relationships typically take the form

$$\log K_d = a \log K_{ow} + \log f_{oc} + b \tag{4}$$

or

$$\log K_d = \alpha \log S + \log f_{oc} + \beta \tag{5}$$

where a, b, α, and β result from regression analysis and are dependent on the solute-sorbent system. The simplicity of (4) and (5) invites their application to any given transport problem. However, the use of (4) and (5) may lead to erroneous estimates of sorption, since the coefficients may vary for different solute-sorbent systems [*Brown and Flagg*, 1981] and, more importantly, these equations may not apply when the organic carbon content is below 0.1% [*Schwarzenbach and Westall*, 1981].

Although linear isotherms are frequently observed for the sorption of nonpolar organic solutes onto natural sorbents, other requirements for use of the retardation factor are less frequently confirmed. In particular, several studies have shown that desorption may be hysteretic [*DiToro and Horzempa*, 1982; *Rao and Davidson*, 1980], while others have shown that the distribution coefficient varies with the solids-to-solution ratio used in the experiment [*O'Connor and Connolly*, 1980; *Horzempa and DiToro*, 1983*a*, *b*; *Voice et al.*, 1983; *Gschwend and Wu*, 1985]. Most recently, *Gschwend and Wu* [1985] and *Voice et al.* [1983] have shown that these deviations can be experimental artifacts related to changes in the composition of the aqueous phase due to suspended organic and inorganic colloidal material that is not removed during centrifugation.

Temperature Dependence

The solubility of a halogenated organic solute in aqueous solution can increase or decrease in response to a change in temperature. This temperature dependence of the solubility has been shown to govern the effect of temperature on the adsorption of nonelectrolytes to inorganic surfaces [*Kipling*, 1965] as well as the partitioning to organic matter in soils and sediments [*Mills and Biggar*, 1969; *Spencer and Cliath*, 1970; *Yaron and Saltzman*, 1972; *Chiou et al.*, 1985]. Since sorption of halogenated organic solutes is inversely proportional to aqueous solubility [*Chiou et al.*, 1979], we may estimate the temperature dependence of the distribution coefficient from solubility-temperature data using

$$K_{d(T_2)} = K_{d(T_1)} S_{(T_1)}/S_{(T_2)} \tag{6}$$

where S is the solubility, and the subscript T_i represents the temperature. In effect, (6) accounts for the variation of the solute activity in aqueous solution with temperature.

MATERIALS AND METHODS

Borden Aquifer Solids

To conduct the laboratory experiments, a large sample of the aquifer material was excavated by the University of Waterloo at a location 21 m from the center of the injection zone and 11.5 m east of the experimental well field at Base Borden, Ontario. Approximately 350 kg of aquifer material was augered to the surface from a depth range of 1–4 m with a 16-cm (6.5-inch) hollow stem auger and then placed in polyethylene-lined containers. The aquifer sample was shipped to Stanford where it was air-dried, homogenized, sieved with a number 4 sieve, and then subsampled with a riffle sample splitter into 448 0.6-kg and 32 1.2-kg subsamples. All subsamples were placed in sterilized whirl pack bags and stored in the dark at room temperature until use.

Mackay et al. [this issue] summarized the known characteristics of the bulk sample of the Borden aquifer material. The important characteristics in the context of this work are that the sorbent has a very low organic carbon content (0.02%), a low specific surface area (0.8 m^2/g), and a low clay content (2% chlorite). While the first two measurements represent the averages of many experimental results and therefore are relatively certain, the 2% chlorite content results from a single X-ray diffraction experiment and therefore must be viewed as a qualitative rather that a quantitative result.

The organic carbon was measured using the Oceanography International ampule system for sediments [*Gershey et al.*, 1979]. To ensure removal of the carbonates, which would have interfered with the analysis, samples were pretreated with concentrated phosphoric acid at 140°C for 30 min. The samples were then spiked with 1 mL of saturated potassium persulfate, sealed in the glass ampule, and autoclaved for 4 hours at 130°C. The carbon dioxide that evolved in the oxidation of the aquifer material during autoclaving was purged from the sample and quantified with an IR detector.

In addition to the information presented by *Mackay et al.* [this issue], several observations of the fine structure of the Borden aquifer material are also of interest in characterizing the aquifer material from the viewpoint of sorption. Black fibrous materials tentatively identified as root hairs, have been observed in the bulk sample and in aggregates obtained from cores taken at the field site. The presence of the roots in cores taken at the site indicates that the fibers are probably not a form of contamination but are in fact present in the aquifer. Small "woody" fragments and shell fragments which are likely porous have also been visually identified.

The presence of root hairs and woody fragments may be significant. It is likely that these contribute to the overall f_{oc}, but, based on the reported inefficiency of the sorption by organic carbon associated with coarse fractions [*Karickhoff et al.*, 1979; *Nkedi-Kizza et al.*, 1983], it is not certain that these materials contribute significantly to sorption.

Simulated Groundwater

A synthetic groundwater was formulated by supplementing organic-free water prepared by a Milli-Q water purification system (Millipore Corporation, Bedford, Massachusetts) with

dominant inorganic ions. To minimize the dissolution of the carbonate minerals present in the aquifer material, the synthetic groundwater was saturated with calcium carbonate at ambient partial pressure of CO_2. The moderate ionic strength of this water also minimized dispersal of particles in the silt and clay size fractions. Neither humic nor fulvic matter were added to simulate the dissolved organic content of the in situ water. The final composition of the synthetic groundwater, presented in Table 1 along with the in situ concentrations, shows that the synthetic groundwater composition closely reflects field concentrations, with the exception of *p*H. Adjusting the *p*H to field conditions was not attempted, as this would have required that the experiment be conducted at higher partial pressures of CO_2.

Organic Solutes

The following radiolabelled carbon 14 tracers were purchased: (^{14}C)-bromoform, 5 mCi/mM; (^{14}C)-carbon tetrachloride, 22 mCi/mM; tetrachloro-(U-^{14}C)-ethylene, 16.9 mCi/mM; hexachloro-(U-^{14}C)-ethane, 18.2 mCi/mM; (Amersham Corporation, Arlington Heights, Illinois) and 1,2-dichloro-(U-^{14}C)-benzene, 8.43 mCi/mM; (Pathfinder Laboratories, Inc., St. Louis, Missouri). Each compound was diluted in methanol, placed in a glass vial equipped with a Teflon-lined cap and stored in the dark at 4°C. Nonradiolabelled carbon tetrachloride, 1,2-dichlorobenzene, hexachloroethane (J. T. Baker Chemical Company), bromoform, and tetrachloroethylene (Aldrich Chemical Company) were used as received after each was screened for purity by gas chromatography. Methanol solutions of each nonradioactive organic solute were spiked with a sufficient quantity of the appropriate tracer to yield a final activity of approximately 500 μCi/μL. Several spiked solutions with concentrations ranging from 0.001 to 0.5 μg/μL were made for each organic solute. Concentrations and purity of the spike solutions were checked periodically by gas chromatography and the radioactivity of each solution was measured for each experiment. Pertinent physical properties of the five halogenated solutes used are presented in Table 2.

Sorption Equilibrium Experiments

Sorption isotherms were measured by the batch technique, in which the amount of sorption is inferred from the change in solution concentration. Since the sorbates are volatile (H_c = 0.02–0.98) and only slightly to moderately hydrophobic (log K_{ow} = 2.3–3.6), and the aquifer material is a weak sorbent (f_{oc} = 0.02%), special precautions were taken to insure that reproducible results could be attained. First, a high solids-to-solution ratio (2.0 g/cm^3) was used to maximize the fractional decrease in solution concentration as a result of sorption. Second, the headspace in the container was minimized by premixing the slurries on rotary tumblers for approximately 3 hours at 12 rpm to completely remove the interstitial air and to disperse a foam that typically formed during the initial mixing. The centrifuge tubes were then completely filled to remove headspace and recapped with the Teflon septum. Finally, carbon 14-labeled solutes were used, because liquid scintillation counting provided a more precise analysis of the supernatant than did solvent extraction followed by gas chromatography.

In the initial phase of the study, various volumes of the spike solutions were injected through the septa to achieve final concentrations that were representative of solution concentrations observed in the field, with the exception of 1,2-dichlorobenzene, for which the maximum concentrations were higher in the field experiment. Subsequent work showed that identical results were obtained by quickly injecting the spike solution into the aqueous phase and immediately capping the centrifuge tube. However, the volume of methanol injected never exceeded 25 μL, which is equivalent to a mole fraction of methanol equal to approximately 0.0004. *Nkedi-Kizza et al.* [1985] have shown that the presence of methanol at this small concentration has a negligible effect on sorption, a finding that was confirmed under the specific conditions of this work [*Curtis*, 1984]. All experiments included a minimum of six blank samples containing no sorbent, which were handled in the manner described above, with the exception that no aquifer material was added to the centrifuge tubes. The samples and blanks were equilibrated at room temperature (21 ± 2°C) on a rotary tumbler at 12 rpm and then centrifuged at 800 G for 30 min. After centrifugation, supernatant samples were analyzed by liquid scintillation counting for 20 min with a Tricarb Model 4530 (Packard Instruments, Downers Grove, Illinois) scintillation counter to determine the aqueous concentration. The equilibrium concentrations were those determined experimentally, whereas the initial concentrations were calculated from the aqueous volume and the spike solution concentration and were adjusted for losses observed in the blanks.

TABLE 1. Composition of the Synthetic and In Situ Groundwater

Constituent	Concentration, μM	
	Synthetic	In Situ*
Potassium	15	3–30
Sodium	220	40–90
Magnesium	139	100–300
Nitrate	15	<10
Sulfate	210	100–300
Chloride	80	30–90
Calcium carbonate	saturated	saturated
*p*H	8.3	7.3
TOC, mg/L	~0.8	10

*From *Mackay et al.* [this issue].

Desorption Experiments

Desorption experiments were conducted by first conducting a typical sorption experiment. After centrifugation, approxi-

TABLE 2. Selected Physical Properties of the Halogenated Organic Chemicals at 20°C

Compound	Log K_{ow}*	S(21)/S(9)†	H_c (−)‡
Carbon tetrachloride	2.7	0.92	0.98
Bromoform	2.3¶	1.06§	0.02
Tetrachloroethylene	2.6	1.00	0.59
1,2-dichlorobenzene	3.4	1.33	0.08
Hexachloroethane	3.6¶	1‖	0.12

*From *Leo et al.* [1971].

†Ratio of aqueous solubilities at 21°C and 9°C, which correspond to the temperatures of the laboratory experiments in this work and of the field experiments [*Mackay et al.*, this issue], respectively; *Horvath* [1983].

‡From *Munz* [1985].

¶From *Curtis* [1984].

§Solubility at 9°C was extrapolated from data at 15°, 20°, and 25°C.

‖Assumed value.

mately 10 mL of supernatant was removed, analyzed, and replaced with synthetic groundwater. The samples were reequilibrated using the same time and mixing conditions used in the equilibration step. After reequilibration, samples were centrifuged and analyzed in the manner used in the sorption experiments. Each sample was subjected to only one desorption cycle; sequential desorption experiments were not possible with this experimental technique because of the losses of the volatile solutes and the weakness of the sorption interactions.

Mass Balance Experiments

To assess the potential problem of losses from the system, mass balance experiments were performed by octanol extraction of the solute sorbed to the sediments. The octanol was introduced into the centrifuge tube with a syringe by injection through the septum to simultaneously displace an equal volume of supernatant, which was removed with a second syringe and analyzed to determine the sorption equilibrium. The remaining slurry was equilibrated with the octanol for 24 hours, followed by analysis of the octanol phase to determine the amount of the solutes extracted from the aquifer material.

RESULTS

Rate Studies

Rate studies were conducted to quantify the approach to equilibrium. Data were obtained by conducting sorption experiments as described above and then analyzing samples at times ranging from 2 to 144 hours. Initial aqueous concentrations used were approximately 30 μg/L. Sorbed concentrations measured in these studies were normalized by the equilibrium concentrations to give the fractional approach to equilibrium values (f), which are presented for all five organic solutes in Figure 1.

All five solutes exhibit the same general uptake behavior: an initial rapid sorption step that occurred in less than 2 hours accounted for approximately 50% of the total sorption, followed by a gradually declining rate for several days. This behavior is similar to that observed by *Karickhoff* [1980]. As the rate study progressed, losses from the blanks gradually increased until after approximately 5 days it became impossible to reliably differentiate between sorption or losses from the system. Therefore the equilibration time was selected as 2 days for carbon tetrachloride, whereas 3 days was selected for the remaining four compounds. These mixing times are equivalent to or exceed those used in several previous studies of hydrophobic sorption of organics onto sediments and aquifer materials [*Chiou et al.*, 1979, 1983; *Karickhoff et al.*, 1979; *Means et al.*, 1980; *Schwarzenbach and Westall*, 1981].

The selection of 2 and 3 days as the mixing times does not guarantee that a state of true equilibrium has been achieved; further sorption could not be quantified if sorption proceeded at rates less than the rate of loss from the blanks. However, the mixing times selected are on the order of the time frame relevant to the early stages of field transport. Unfortunately, longer-term rate experiments, although pertient to the field transport, could not be conducted with the experimental technique described here.

Sorption Equilibrium Studies

Three typical isotherms, those for carbon tetrachloride, tetrachloroethylene, and 1,2-dichlorobenzene, are presented in Figure 2. The isotherm for hexachloroethane nearly coincides with that for 1,2-dichlorobenzene and the isotherm for bromoform coincides with that for carbon tetrachloride and therefore have been omitted for clarity. Error bars presented in Figure 2 represent the results of error propagation calculations conducted to estimate the uncertainty in the calculated quantities that results from the uncertainties in all of the measured quantities and the losses in a minimum of six replicate blanks. Errors from these two sources were of the same magnitude.

Three models have been fitted to the data using the method of least squares. These models include the standard linear regression, a linear model in which the intercept has been suppressed (i.e., forced through the origin), and a linear fit to a log-transformed data (the Freundlich model). Results from these least squares analyses are summarized in Table 3. All equilibrium data can be fit quite well by the standard linear model, as is shown by the coefficient of determination near unity and the random scatter of the data about the regression line.

Desorption Results

A sorption and desorption isotherm for hexachloroethane is presented in Figure 3. The desorption isotherm is systematically displaced upward slightly, suggesting a small degree of irreversibility, although these differences are not statistically significant in view of calculated error bars and the standard linear regression results. Additional desorption studies were attempted with bromoform. Unfortunately, the sorption interactions were too weak to permit precise quantitation of the amount of the solute desorbed in light of the observed losses.

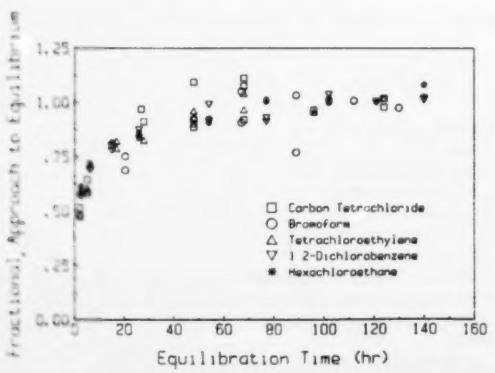

Fig. 1. Fractional approach to equilibrium over time for carbon tetrachloride, bromoform, tetrachloroethylene, 1,2-dichlorobenzene, and hexachloroethane.

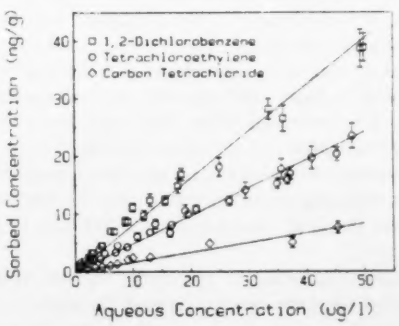

Fig. 2. Sorption isotherms for carbon tetrachloride, tetrachloroethylene, and 1,2-dichlorobenzene.

TABLE 3. Summary of the Isotherm Data and Statistical Analysis

	CTET	BROM	PCE	DCB	HCE
Number of data	11	10	25	24	52
C_{max}, ng/cm^3	47	13	49	50	34
Linear, with intercept					
K_d, 95% CI	0.15 ± 0.03	0.17 ± 0.02	0.45 ± 0.02	0.76 ± 0.03	0.81 ± 0.03
Intercept, 95% CI	0.41 ± 0.53	−0.49 ± 1.17	0.82 ± 0.57	1.26 ± 0.59	−0.09 ± 0.53
R^2	0.948	0.981	0.987	0.992	0.981
MS_e*	0.545	0.093	0.781	1.03	1.08
Linear, with suppressed intercept					
K_d, 95% CI	0.17 ± 0.03	0.17 ± 0.02	0.48 ± 0.02	0.81 ± 0.03	0.81 ± 0.03
R^2	0.972	0.992	0.994	0.993	0.981
MS_e	0.629	0.098	0.927	1.42	1.08
Freundlich					
K_f, 95% CI	0.25 ± 0.0	0.15 ± 0.02	0.93 ± 0.00	1.16 ± 0.00	0.82 ± 0.00
Exponent	0.89 ± 0.11	1.03 ± 0.12	0.79 ± 0.07	0.91 ± 0.03	0.99 ± 0.03
R^2	0.975	0.979	0.960	0.994	0.992
MS_e	0.540	0.097	1.172	0.99	1.10

*Root-mean-square residual.

Effects of Dissolved Humic Material

During a typical sorption experiment, the concentration of the dissolved organic carbon (DOC) increased from an initial value of 0.8 mg/L to an average final concentration of 20 mg/L. There are two possible effects of this increase in DOC in the supernatant: (1) diminished sorption capacity resulting from desorption of the organic matter and (2) binding of small organic solutes to the suspended humic materials.

Typical sorption experiments were conducted at a solids-to-liquid ratio of approximately 2 g/cm^3 in 40-mL centrifuge tubes, which is equivalent to 45 g of aquifer material equilibrated with 22 cm^3 of synthetic groundwater. For the DOC of the water to increase from 0.8 to 20 mg/L, the aquifer material would have to lose 0.42 mg or approximately 5% of its organic carbon. Suspended humic material can bind or complex small molecules in solution to lower their activity and therefore decrease the extent of sorption [*Chiou et al.*, 1984, 1985; *Karickhoff*, 1984; *Gschwend and Wu*, 1985]. Although the binding constants between the nonpolar solutes and the dissolved humic material are not well known, *Karickhoff* [1984] suggested that the octanol-water partition coefficient can be used as an upper bound. If hexachloroethane behavior is used again as the criterion, we expect that the dissolved organic carbon has less than a 5% change in K_d due to the dissolution of the organic matter. If we assume that all of the sorption is associated with the organic carbon (to be discussed below), then the combined effects of diminished sorption capacity and solubilization should decrease the K_d of hexachloroethane by at most 10%. Even smaller effects are expected for the remaining solutes used in this study.

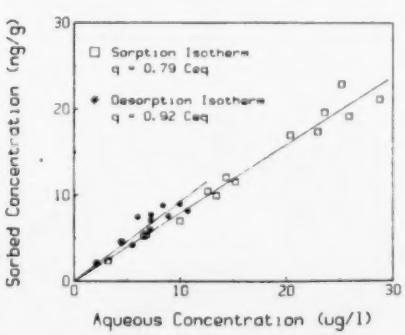

Fig. 3. Sorption and desorption isotherm for hexachloroethane.

Mass Balance Experiments

The results from the octanol extractions along with the recoveries in the blanks are presented in Table 4. In general, the percent lost from the blanks increased with increasing Henry's constant; the trend was opposite with reference to K_{ow}. These opposing trends suggest that the losses from solution are probably due to volatilization rather than to sorption onto the glass walls or the septum.

The results from the octanol extraction experiments are similar to the results from the blanks. The incompleteness of the octanol extraction recoveries may stem from octanol being an imperfect extractant, although this effect is probably small, since solvents with solubility parameters similar to that of octanol have been shown to be good extractants for hydrophobic solutes sorbed to humic materials [*Freeman and Cheung*, 1981]. The extraction efficiencies of less than 100% may also result from losses resulting from volatilization. The important result from the mass balance experiments is that most of the solute that had disappeared from solution and was attributed to sorption was at least still in the centrifuge tube. Since the results from the blanks suggest that adsorption to glass walls or the septum is probably negligible, the octanol

TABLE 4. Percent of the Solute Recovered From Blanks and Octanol Extracts

Compound	Blank, %	Octanol, %
CTET	93 ± 2	92
BROM	95 ± 2	not determined
PCE	93 ± 2	91
DCB	94 ± 3	94
HCE	96 ± 2	95

can be presumed to have extracted most of the organic solute from the sorbent.

DISCUSSION

The near-zero intercepts determined from linear regression results suggest that a regression through the origin may be appropriate. Indeed, we can expect the isotherm to pass through the origin, since the sorbed concentration must equal zero if no solute were added to the system. A nonzero intercept is therefore an indication of nonlinearity in the isotherm. To best assess the two linear models, we may compare the root-mean-square residual of the regression defined as [*Montgomery and Peck*, 1982]

$$MS_e = \left(\frac{\sum e_i^2}{\nu}\right)^{1/2} \tag{7}$$

where e_i and ν are the residuals and the degrees of freedom, respectively. Comparison of the MS_e values, which are included in Table 3, leads to the conclusion that the standard linear model including the intercept fits the observed data slightly better than does the linear model with suppressed intercept.

Use of the linear regression technique is not statistically rigorous, given that the variance in the dependent variable is not distributed uniformly throughout the observed concentration range. Typically, it is more appropriate to conduct a linear least squares fit on the log-transformed data, since the transformation results in a closer approximation to the uniform distribution of variance [*Bowman et al.*, 1984]. The results from this regression, which amounts to fitting the Freundlich isotherm to the data, are also included in Table 3. The Freundlich model also fits the data quite well, as suggested by the values of the coefficient of determination being near unity. The fact that both of the linear models fit the data well indicates that there is not a great amount of curvature in the data. Indeed, the exponents in the Freundlich model range from 0.794 to 1.04 and three exponents, those for carbon tetrachloride, bromoform, and hexachloroethane, are not statistically different from unity at the 95% confidence level. The difficulty in distinguishing between the Freundlich and linear fits is compounded by the narrow range in the experimental data. The aqueous concentration ranges over a factor of 50 at the most and therefore only sharply nonlinear isotherms will not be adequately fit by the linear approximation.

Deviations between sorbed concentrations calculated from the Freundlich and the linear regression through the origin are presented in Table 5 as the ratio of the two calculated sorbed concentrations. The largest deviations occur at 1 μg/L for tetrachloroethylene, which has an exponent the furthest from unity. However, the values of the MS_e for the two different regressions reveal that the two models are equally suitable.

For the purpose of the remaining discussion, we adopt the results from the regression through the origin for the following reasons: (1) the narrow range in concentration makes it difficult to distinguish between departures from linearity and random scatter in the data; (2) the Freundlich isotherm does not result in a significantly better fit than the linear model; and (3) the linear model with suppressed intercept is most convenient in applying (2) to estimate solute mobility, as it corresponds to a constant retardation factor.

Evaluation of Sorption Models

The observation of a linear isotherm with a zero intercept is not sufficient to confirm that the sorption mechanism is partitioning into the organic matter [*Chiou et al.*, 1985]. Several different sorption models, including the Langmuir, the BET, and the Freundlich, cannot be distinguished from linear isotherms over narrow intervals and at small values of the relative concentration C_{eq}/S, where S is the solubility. For the compounds included in this work, the least soluble is hexachloroethane, which, even at the maximum equilibrium concentrations achieved in the sorption studies of 50 μg/L, corresponds to only 1% of solubility. Therefore the fact that all isotherms determined in this study are essentially linear throughout the concentration range studied does not constitute a confirmation of the partitioning theory.

To assess the applicability of the organic matter partitioning model, we may compare the organic carbon partition coefficients resulting from the present work with estimates based on previous empirical correlations. Organic carbon partition coefficients K_{oc} for the organic compounds used in this study were correlated with the octanol-water partition coefficients as shown in Figure 4. The correlation, which extends over less than 2 orders of magnitude in K_{ow} and includes only five compounds, has a relatively small coefficient of determination (0.64) and a slope less than the slope determined in several previous investigations [*Karickhoff et al.*, 1979; *Schwarzenbach and Westall*, 1981], where partitioning into the organic matter was presumed to occur, as is shown in Figure 4. The deviations between the observed data and correlations are the least, albeit marginally, when the regression by *Karickhoff et al.* [1979] is used for comparison. Nevertheless, the observed K_{oc} values exceeded the estimated values by factors which ranged from a maximum factor of 10 for tetrachloroethylene to a minimum of 1.7 for hexachloroethane.

TABLE 5. Ratios of Sorbed Concentrations Calculated From the Freundlich and Linear Equilibrium Models

Solute	Concentration, μg/L		
	1	25	50
CTET	1.49	1.06	0.98
BROM	0.91	1.01	1.04
PCE	1.95	1.00	0.87
DCB	1.43	1.06	0.99
HCE	1.01	0.99	0.98

Ratio of sorbed concentrations is defined as the ratio of calculated sorbed concentrations (Freundlich model to intercept-suppressed, linear model) at the same solution concentration.

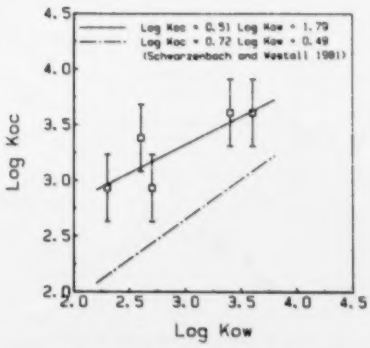

Fig. 4. Correlation between the distribution coefficient and the octanol water partition coefficient.

The fact that the observed organic matter partition coefficients are larger than those estimated could result from several possible effects including 1) an error in the organic carbon content measurements; 2) greater hydrophobicity of the organic matter from the Borden aquifer compared to the sediments and soils on which the generalized partitioning correlations are based; 3) sorption contribution from the mineral surface; or 4) any combination of the above. The error bars in Figure 4 illustrate that even a factor of two error in f_{oc} fails to account for the deviations. The possibility that the organic matter is more hydrophobic than that from soils and sediments seems unlikely, because the slope, which is a measure of the hydrophobicity of the organic phase [*Leo et al.*, 1971], is less than that observed in previous studies, where partitioning to the organic phase was believed to dominate. The anomalously large partition coefficients probably result from adsorption to mineral surfaces, which would be consistent with the findings of *Schwarzenbach and Westall* [1981] for low organic carbon sorbents.

Comparisons With Field Observations

To make comparisons between the field and laboratory data, we chose to calculate the retardation factor R for both sets of data. The observation of a reversible, linear isotherm in itself is not sufficient to ensure that the retardation factor approach (i.e., equation (2)) is valid. It is equally important that the distribution coefficient for the solute of concern be independent of other migrating solutes [*Reardon*, 1981; *Valocchi et al.*, 1981]. Fortunately, partitioning of nonpolar organics onto natural sediments is believed to satisfy the required conditions of linearity, independence of other solutes, and 'independence of solution characteristics such as ionic strength and pH [*Chiou et al.*, 1984; *Karickhoff*, 1984].

To correct for the temperature difference between the field observations (9°C) and the laboratory experiments (21°C), we have estimated K_d at the field site temperature using (6) and the solubility temperature data from *Horvath* [1983]. The ratios of the estimated solubilities at 21° and 9°C are presented in Table 2. This ratio ranges from 0.92 for carbon tetrachloride to 1.35 for 1,2-dichlorobenzene. Because no solubility-temperature data were found for hexachloroethane, a value of unity was assumed for the solubility ratio.

Despite the low organic carbon content of the sorbent, distribution coefficients were estimated from the empirical regression presented by *Schwarzenbach and Westall* [1981] as the sorbents and solutes used in that study were the most similar to those in the current study. The estimated distribution coefficients were then adjusted for the lower field temperature in the manner described above. The retardation factors were calculated using (2) with the bulk density and porosity taken as 1.81 ± 0.045 g/cm^3 and 0.33 ± 0.017, respectively [*Mackay et al.*, this issue].

Table 6 presents a summary of the retardation factors determined from the laboratory and field studies. The retardation factors from the laboratory results are presented along with the standard deviations resulting from the uncertainty in K_d, the bulk density, and the porosity and an assumed uncertainty in the solubility ratio of 10%. The ranges of temporal field retardation factors represent the ranges of observed values at three sampling wells, with the exception of hexachloroethane, for which reliable quantitation was possible at only one of the monitoring points, e.g., point b in Table 1 of *Roberts et al.* [this issue]. The retardation factors presented for the spatial data are those calculated from ratio of instantaneous velocities for the chloride and organic plumes, respectively [*Roberts et al.*, this issue, Table 5].

TABLE 6. Comparison of Retardation Factors

	Predicted*	Batch Experiments	Field Data†	
			Temporal	Spatial
CTET	1.3	1.9 ± 0.1	1.6–1.8	1.8–2.5
BROM	1.2	2.0 ± 0.2	1.5–1.8	1.9–2.8
PCE	1.3	3.6 ± 0.3	2.7–3.9	2.7–5.9
DCB	2.3	6.9 ± 0.7	1.8–3.7	3.9–9.0
HCE	2.3	5.4 ± 0.5	4.0	5.1–7.9

*Calculated from the regression by *Schwarzenbach and Westall* [1981] with $f_{oc} = 0.02\%$.
†From Tables 1 and 5 of *Roberts et al.* [this issue].

The retardation factors predicted from empirical correlations are substantially smaller than the experimental estimates of retardation, as is shown in Figure 4 and in Table 6. The lack of agreement is independent of the empirical $K_{oc} - K_{ow}$ or $K_{oc} - S$ relationship used. This deviation is attributed to the fact that the empirical correlations do not take into account the mineral surface contribution to sorption, as discussed above in connection with Figure 4.

The agreement between the laboratory results and the retardation factors inferred from the temporal data is quite good for carbon tetrachloride, bromoform, and tetrachloroethylene: in all three cases the laboratory-estimated retardation factors agree with the field observations within experimental error (Table 6). For hexachloroethane, the laboratory estimate of retardation exceeds the single reliable temporal estimate of field retardation by 35%. This difference is within reason, given the error in the retardation factor, the lack of solubility-temperature data, and the error of estimate of the field data. The agreement for 1,2-dichlorobenzene is not as close; the laboratory-derived estimates of retardation exceed the temporal field observations by up to a factor of 4. However, the interpretation of the temporal data for 1,2-dichlorobenzene was confounded by the transformation of the compound, which resulted in quite small concentrations at the sampling wells and cast doubt on the quantitative estimates of the temporal retardation factor [*Roberts et al.*, this issue].

The retardation factors estimated from the spatial analysis range from a minimum nearest the injection zone to a maximum when the plumes were farthest from the injection zone in space and time [*Roberts et al.*, this issue, Figure 8]. The comparison between the laboratory data and retardation factors inferred from the spatial data reveals that the estimates of retardation based on the laboratory results agree within experimental error with the lower end of the range of spatial retardation factors in the cases of carbon tetrachloride, bromoform, and hexachloroethane. The laboratory estimate for tetrachloroethylene exceeds the minimum spatial retardation by 33%, and that for 1,2-dichlorobenzene corresponds approximately to the midrange of the spatial results. For all five solutes the maximum spatial retardation factors, which correspond to the maximum distance and time from the injection are approximately 30–65% greater than laboratory estimates. Deviations at the greatest distance from the injection zone may result from sorptive interactions that were not detectable with the laboratory techniques used in this study, perhaps because of a slow diffusive uptake from solution. It is plausible that carbonate or sandstone grains which are present in the

aquifer material can possess internal porosity as well as organic matter [*Blatt et al.*, 1981], and hence could contain sorption sites reached only by a slow diffusive process. These complications notwithstanding, the comparison of the retardation factors clearly demonstrates that sorption does explain the observed field retardation for the temporal and spatial data.

SUMMARY AND CONCLUSIONS

Laboratory studies have been conducted to measure the sorption of five organic chemicals used in the Borden field study with aquifer material excavated 11.5 m from the experimental well field. The isotherms measured were all essentially linear throughout the concentration ranges studied and, at least for hexachloroethane, appeared nearly reversible for practical purposes. In all cases more sorption was measured than would be predicted from previously published empirical relationships, consistent with sorption of the organic solutes onto the mineral surfaces at low organic carbon contents. The retardation factors inferred from the observed distribution coefficients were in generally good agreement with observed temporal and spatial field data. The agreement is closest nearest the injection wells, as these field data are probably least likely influenced by degradation or a slow diffusive uptake that could not be monitored by the laboratory technique used in this study. In all cases, the maximum spatial retardation factors exceed the laboratory estimates.

The close agreement between field and laboratory results does not imply that the linear, reversible equilibrium model has been adequately confirmed as a general rule. The close agreement between the two results may be partly due to the nature of the field site. The Borden aquifer was chosen as the experimental site in part because of its relative simplicity: the aquifer is relatively homogeneous and the flow is nearly uniform. Thus the experiments were conducted under nearly ideal conditions. It remains to be seen whether such close agreement can be obtained in a more complex hydrogeological setting.

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G. P. Curtis, M. Reinhard, and P. V. Roberts, Department of Civil Engineering, Stanford University, Stanford University, Stanford, CA 94305.

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